CHARACTERIZATION OF CROSSLINKED SODIUM TRIMETAPHOSPHATE STARCH FROM OIL PALM TRUNK AND ITS SUITABILITY AS PARTICLEBOARD BINDER

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LIST OF SYMBOLS AND ABBREVIATIONS

g/cm^3	gram per centimetre cubic
ºC	Degree Celsius
cm	centimetre
MPa	Mega Pascal
mm	millimetre
N/mm^2	Newton per millimetre square
%	Percentage
mL	millilitre
mPa.s	milli Pascal second
UF	Urea formaldehyde
PF	Phenol formaldehyde
MF	Melamine formaldehyde
pMDI	polymeric methylene diphenyl diisocyanate
STMP	Sodium trimetaphosphate
STMP-starch	Cross-linked oil palm trunk starch with sodium trimetaphosphate
STMP-UF	13 % STMP-Starch mix with 2 % UF
OPT	Oil palm trunk
GOPOD	glucose peroxide-oxidase

JIS	Japanese Industrial Standard
BS	British Standard
ASTM	American Society for Testing and Materials
MOR	modulus of rupture
MOE	modulus of elasticity
IB	internal bond strength
VOCs	volatile organic compounds
CARB	California Air Resources Board
FTIR	Fourier transform-infrared spectroscopy
XRD	X-ray diffractometry
TGA	Thermogravimetric analysis
SEM	Scanning electron microscopy

PENCIRIAN KANJI DARIPADA BATANG KELAPA SAWIT TERPAUT SILANG BERSAMA NATRIUM TRIMETAFOSFAT DAN KESESUAINNYA SEBAGAI PEREKAT BOD PARTIKEL

ABSTRAK

Objektif kajian ini adalah untuk menilai beberapa sifat bod partikel dibuat menggunakan kanji batang kelapa sawit terpaut silang bersama natrium trimetafosfat untuk dijadikan perekat. Panel eksperimen tiga lapisan, telah dihasilkan daripada campuran *Acacia mangium* dan kayu getah. Panel telah dihasilkan berdasarkan dua ketumpatan sasaran 0.60 g/cm^3 dan 0.80 g/cm^3. Panel menggunakan urea formaldehid, kanji asli batang kelapa sawit dan kanji terubahsuai natrium trimetafosfat dicampur dengan 2 % urea formaldehid sebagai perekat juga telah dinilai. Panel telah dinilai di atasnya sifat-sifat fizikal dan mekanikal. Di samping itu, Termogravimetri, diffraktometri x-ray dan analisis mikroskopik telah dijalankan untuk menilai sifat-sifat perekat. Beberapa analisis anggaran pada perekat juga telah dilakukan. Panel eksperimen dengan ketumpatan 0.80 g/cm^3 menunjukkan sifat mekanikal dan fizikal yang lebih baik berbanding dengan ketumpatan 0.60 g/cm^3. Penambahbaikan dalam sifat-sifat mekanikal dan fizikal juga dipamerkan oleh panel yang dihasilkan menggunakan kanji batang kelapa sawit diubahsuai dengan natrium trimetafosfat sebagai perekat, dengan tambahan sebanyak 2 % urea formaldehid panel tersebut menunjukkan sifat-sifat yang lebih baik dan memenuhi tahap minimum untuk sifat-sifat mekanikal dan fizikal menepati piawaian Japanese Industrial Standard (JIS A5908) untuk bod partikel jenis 8.

CHARACTERIZATION OF CROSSLINKED SODIUM TRIMETAPHOSPHATE STARCH FROM OIL PALM TRUNK AND ITS SUITABILITY AS PARTICLEBOARD BINDER

ABSTRACT

The objective of this study was to evaluate some properties of particleboard made using oil palm trunk starch crosslinked with sodium trimetaphosphate as a binder. Three-layer experimental panels were manufactured from homogenous mixture of *Acacia mangium* and rubberwood. Panels were produced based on two target densities of 0.60 g/cm^3 and 0.80 g/cm^3. Panels using urea-formaldehyde, native oil palm trunk starch and sodium trimetaphosphate modified starch mixed with 2 % urea formaldehyde as binder also have been evaluated. Panels were evaluated based on physical and mechanical properties. In addition, thermogravimetric, x-ray diffractometry and microscopic analysis were carried out to evaluate the properties of the binder. Some proximate analysis on binder also have been done. Experimental panel with 0.80 g/cm^3 density showed better mechanical and physical properties as compared to panel having 0.60 g/cm^3. Improvement in mechanical and physical properties also showed by the panel produced using modified oil palm trunk starch with sodium trimetaphosphate as binder, with addition of 2 % urea formaldehyde that panels showed better properties and meet the minimum requirement for internal bond (IB) strength, Modulus of Elasticity (MOE) and Modulus of Rupture (MOR) as stated in Japanese Industrial Standard (JIS A5908) for Type 8 particleboard.

1 INTRODUCTION

1.1 Research background

The wood-based industry is one of the resource-based industries, which has progressed tremendously and has a potential for growth. It is a major contributor to export earnings and employment in the manufacturing sector. The industry has diversified into the production of downstream products, including laminated veneer lumber, medium density fibreboard, and particleboards. The increasing demand of wood and wood-based products and mismanagement of current resources and unsustainability of deforestation, cause the industry to focus more on panel product such as particleboard, chipboard, and fibreboard. Since 2012, Malaysia no longer exports unprocessed wood products (Malaysian-German Chamber of Commerce and Industry, 2012).

The demand for engineered composites, such as particleboards are getting higher and becoming focus in wood and wood-based industry. In line of it growth, concern on formaldehyde emissions is getting louder. Particleboards are mostly produced using formaldehyde-based resin as the binder. Most commonly, urea formaldehyde (UF) is used due to its low cost and exceptional properties (Pizzi, 2015). During particleboard making process, harmful formaldehyde gas will be released. Formaldehyde emission from wood-based panel may cause irritation to upper respiratory tract nose and eyes (Conner, 1996).

Regarding the negative effect of formaldehyde-based adhesive application and rising of public concern on environment and health, various research and development were carried out in order to produce a composite panel with good physical and mechanical characteristic without compromising the health and environmental aspect. One of the approaches toward this goal is the application of natural-based adhesive.

In wood-based composite industry, the most commonly use natural adhesive are lignin, tannin and starch. In general, natural-based adhesives are sensitive toward moisture as compared to the synthetic adhesive, most natural-based adhesive are sensitive toward moisture (Suárez, 2011). Therefore, modifications need to be done to natural adhesive in order to create natural-based adhesives with performance matching those synthetic adhesives. From the previous work by Pan et al., (2006) mixed adhesive from rice bran and polymeric methylene diphenyl diisocyanate (pMDI) has produced a panel that had equal performance as panel produced from only pMDI as adhesive.

The major intention of this research is trying to reduce the utilization of formaldehyde-based adhesive in wood-based composite panel manufactured by introducing a green adhesive that produced from oil palm trunk starch. It is also in line with the government's Third Industrial Master Plan (IMP3) 2006-2020, towards improvement on quality and minimization of waste and enhancing the green image of Malaysian wood and wood-based industry. The oil palm trunk has been chosen as the source of starch for adhesive making because of there are plenty of oil palm trunk waste in Malaysia. Malaysia is a main producer and exporter of palm oil. About 365,000 ha of oil palm planting are capped by 25-37 years old trees, and oil palm plantation will generate approximately 126, 000 ha of old trees per year over next ten

years (Ulbrich et al., 2015). Oil palm industry will generate a bigger amount of oil palm trunk (OPT) waste, and most them are left to decay or burned (Sumathi et al., 2008). Those OPT waste can be utilized as starch resource of as a green adhesive for particleboard making.

There are various types of starch modification and have been generally categorized into four categories which are physical, chemical, enzymatic and genetic modification (Kavlani et al., 2012). In this study, starch have been cross-linked with sodium trimetaphosphate (STMP). This chemical modification technique were carried out-based on the previous starch modification work by Chatakanonda et al., (2000). According to that study, the addition of phosphate group from STMP increased the stability of starch molecules toward heat and decreased the swelling of starch. This modification technique is usually used in food industry, where modified starches are commonly used as food thickener, due to their non-toxicity. The potential of crosslinking oil palm trunk starch with STMP was investigated in this study. In addition, the suitability of cross-linked STMP-starch as binder for three-layer particleboard panel was also evaluated.

1.2 Research Objectives

The objectives of this study were:

I. To characterize and compare properties of native starch and STMP-starch derivative after crosslinking process with STMP.

II. To evaluate the mechanical and physical properties of particleboard produced from modified starch (STMP-starch) as binder.

2 LITERATURE REVIEW

2.1 Particleboard

From the ancient time, around 2000 B.C., Egyptian had already discovered a way to produce ancient plywood from thin wood slat (Navi and Sandberg, 2012). The first concept of producing wood-based composite products similar to the modern particleboard was discovered in 1887. Due to the shortage of the lumber at the end of 1940s, the use of plywood was replaced with the particleboard. The first commercial panel were manufactured during World War II at a factory in Bremen, Germany by the Torfit-Werke G.A heske (Kloeser et al., 2007).

Naturally, solid wood has one major disadvantage. The strength is longitudinal to the fibre direction, while the strength across the fibre is too weak. (Madsen and Gamstedt, 2013). Particleboards are produce by pressing and gluing homogenized raw materials in different directions to produce wood panel product with homogenized dimensional stability. Other advantage of using wood composites products is optimization of wood material. It will generate less waste as wood composite are fabricated from wood chips and small particles.

Particleboard is the major type of wood composite produced, which is cover 62 % of European panel board production in 2006 (Barbu and van Riet, 2008). Particleboard is described as wood-based panel produced under pressure and heat from wood particles usually with the addition of a binder. The common type of particle uses in producing particleboard are wood shavings, flakes, wafers, chips, sawdust and wood wool. Sometimes, the term particleboard is also generally including waferboard and oriented strandboard, which are manufactured primarily from wood flakes and wafers.

The particleboard industry minimize waste and residue from other wood-based industries such as sawdust and wood chips by converting a huge quantity of those waste into particleboard panels.

2.2 Particleboard manufacturing

Particleboards are usually manufactured in panel form. However for certain purposes, moulded particleboards are also produced. Particleboards usually produced in single or multi-layer form. Generally, multi-layer particleboards are manufactured in three or five layers. The outer layer is usually know as face layer, and the inner layers is referred to as core layers. For smooth finishing face particles are finer than core particles.

Industrial scale particleboard manufacturing process begins from the selection of raw material. Raw material can be generated onsite or shipped to the mill. Furnish is usually in the form of wood chips, sawdust and planer shavings. For onsite raw material, logs are debarked and cut into a proper size and chipped. After shipping the offsite and the onsite furnish may be further reduced in size using the hammermills, refiners, or flakers. After that, those raw materials will be screened and classified according to their sizes. Those material are classified based on length and thickness to separate the face and core particles before there are been transported to storage bins.

Next, those particles are dried to reduce their moisture content to the range of 2 % to 8 %. Those classified furnish of core and face material are conveyed to dryers. The most common type of dryer used in the particleboard industry is rotary dryer. Dryer inlet temperatures may vary depending on the moisture content of the particles. For wet furnish, usually with moisture content up to 50 %, predryer could

be used for initial drying. The moisture content of furnish can be controlled by adjusting the dryer inlet temperature, usually the core particle are required at lower moisture content.

After the completion of drying process, those particles will pass through a cyclone before moved to holding bins. Usually, before storage in the holding bin, face particles are screened to eliminate fines or dust, which tend to absorb too much of binder. From the holding bins, furnish were blended with binder, wax and other additives in mixer. The resinated particles are transferred to the forming machine via a belt conveyer, which spread the mixture in form of continuous mat. By mean of air, former spread resinated particles into an air chamber before they float down into position through a moving screen to form a homogenous mat. Mats formed may be prepressed before trimming and pressing process. Prior to pressing, mats formed are trimmed and cut into required length and sizes. To activate and cure the binder, heat and pressure are applied to form a firm bonding between fibres to form solid panels. Most particleboard plant applied a multi-opening batch press rather than single-opening press. Total pressing time is vary, from 2.5 minutes for single-opening press and up to 6 minutes for multi-opening presses and also depend on the pressing temperatures. Common temperature range applied for pressing is between of 149 $^{\circ}$C to 182 $^{\circ}$C.

Panel produced are cooled to prevent decomposition of cured adhesive. After cooling, panel are sanded and trimmed to desired sizes. Residue from those proses will be recycled or burnt to generate a steam in the onsite boiler for heating process. After trimming, finishing process such as laminating or veneer application are done before it packaging and reach the market.

Application of particleboards in furniture and construction industry was huge, due to their low cost and fabricated properties. Generally, there are three factors which may affect the properties of panel produced. Target density of the panel, amount of adhesive used and dimensional size of the particles used (Abdul Khalil and Rozman, 2004). Due to these factors, manufacturer can fabricate the particleboard to the desired cost and end use. There are various types of specification and classification of particleboards based on Japanese Industrial Standard (JIS), British Standard (BS) and American Society for Testing and Materials (ASTM). The classification of particleboard are vary and based on different parameters like mechanical properties, formaldehyde emission and others. For example Table 2.1 shows the classification of particleboard based on bending strength as classified by JIS 2003.

Table 2.1 Classification of particleboard based on the bending strength (JIS, 2003)

Classification		Symbol	Bending Strength
Base particleboard and decorative particleboard	Type 18	18	The bending strength must be 18.0 MPa or more both lengthwise and width wise
	Type 13	13	The bending strength must be 13.0 MPa or more both lengthwise and width wise
	Type 8	8	The bending strength must be 8.0 MPa or more both lengthwise and width wise
Base particleboard	Type 24-10	24-10	The bending strength must be 24.0 MPa or more lengthwise and 10.0 MPa or over width wise
	Type 17.5-10.5	17.5-10.5	The bending strength must be 17.5 MPa or more lengthwise and 10.5 MPa or over width wise
Veneered particleboard	Type 30-15	30-15	The bending strength must be 30.0 MPa or more lengthwise and 15.0 MPa or over width wise

2.3 Types of particles

Quality of produced particleboards depends on many factors, one of them is types of particles used (Abdul Khalil and Rozman, 2004). Density of wood species used for the particleboard manufacturing is the most crucial characteristic in wood particle selection as it effect the density of panel produced (Hrázský and Kral, 2003). Density of wood particles chosen may also effect the essential strength of panel. Other than density of wood species selected, size and geometry of wood particle are also one of the fundamental characteristic need to be accounted (Gozdecki et al.,

2015). Low density wood particle is preferred in most panel production, it give superior glue to particle contact, better particle conformation and reduced uneven density. When pressed, low density wood particle is easy to rupture and give a good particle conformation and increase the contact between particles hence optimise the consumption of adhesive used (Hrázský and Kral, 2003).

In Malaysia, *acacia mangium* was first planted in Sabah in 1966 (Sahri et al., 1993). This fast growing tree was planted in Malaysia and Indonesia under forest plantation program (Hoong et al., 2009). In Malaysia, *acacia mangium* plantation cover about 50 249 hectares of land area and it is also naturally grown along site of river banks, in mangrove area and road tracks (Wan Nadhari et al., 2014). *Acacia mangium* has rapid early grow, annual diameter growth is up to 5 cm in average and increasing height up to 5 m in the first 4-5 years. This tree is not appropriate for timber production since it has flutes and knots but suitable for making excellent particleboard with good dimensional stability and great physical properties (Korai et al., 2000).

Nowadays, rubberwood or also scientifically known as *Hevea brasiliensis* is getting popular and one of important material of wood for Malaysia timber and wood-based composite industry. Rubberwood is an alternative for substituting and reducing the reliance of wood industry on the other wood species which are more expensive (Hoong et al., 2009). Rubberwood was first planted in Malaysia during British colonial era in 1879 at Kuala Kangsar, Perak (Ratnasingam and Ioras, 2003). Since then, it become one of Malaysian important commodity and planted for latex. In 2009, Malaysia has approximately 1.47 million hectors of rubber plantation (Shigematsu et al., 2011). Normally, less economic 25 to 30 years old rubber trees

are selected for logging because, old rubber trees are less economic because the latex production was decrease. A low quality of rubber wood are low-cost and have short fibre length which are suitable for particleboard and other wood-based composite panels making (Hiziroglu et al., 2004). On the other hand, rubber wood composite panels passed numerous standard requirements and have a great market values (Izran et al., 2011).

2.4 Adhesive

In wood-based industry, adhesives are normally thermosetting polymers used to bind wood particles to form a wood-based panels, while adhesive strength is defined as the force needed to dissociate the substrates that are bind together (Frihart, 2005). Natural adhesives were discovered a long ago and had been broadly use for vast application and experience a lot of changes and improvement. Adhesives for wood-based products can be classified in two major groups which are synthetic adhesives and natural-based adhesives.

2.4.1 Synthetic adhesive for wood-based products

There are various types of wood-based composite adhesives, but the most popular and commonly used is formaldehyde-based adhesives. These adhesives are based on formaldehyde with phenol, resorcinol, urea, melamine, or mixtures of those compounds. Each of those formaldehyde-based adhesive has its own unique characteristic that made it suited for different applications (Pizzi and Mittal, 2003). Formaldehyde-based adhesives are thermoset adhesives. The curing process occurs by formaldehyde linking the reactive sites on different chains (Frihart, 2005). Few examples of formaldehyde-based adhesive and formaldehyde emission are discussed later.

Other types of adhesive are isocyanate-based adhesive. Isocyanates contains reactive groups such as amine and alcohol groups, this permit a self-polymerize or react with variety of monomers. The polymerization process will occur rapidly and at high conversion rate (Pizzi and Mittal, 2003). However, isocyanates can easily react with water molecules in wood and competing with cellulose and hemicellulose. In addition, safe handling of isocyanates is also a concern, due to the ability of isocyanates to react promptly with many compounds exist in human bodies. The most conventional isocyanates adhesive is polymeric diphenylmethane diisocynates (pMDI). It is a self-curing isocyanates adhesive and generally used for oriented strandboard (OSB). Another example and conventional isocyanates adhesive are emulsion-polymer isocyanate (EPI or API), polyurethane adhesive. Other major types of synthetic adhesives are epoxy adhesive and vinyl acetate dispersion adhesive (Pizzi and Mittal, 2003).

2.4.1.1 Urea Formaldehyde adhesive

Urea formaldehyde (UF) adhesive is the standard adhesive used in the wood-based industry. Figure 2.1 shows the molecular structure of UF. It is the most desirable adhesive because of low cost and produced high strength of wood-based composite products. UF adhesives are known as exceptional thermosetting adhesives and it also the most widely formaldehyde adhesive produced in the entire world (Frihart, 2005). UF adhesives are also broadly used in other industries like textile, paper and automotive industries.

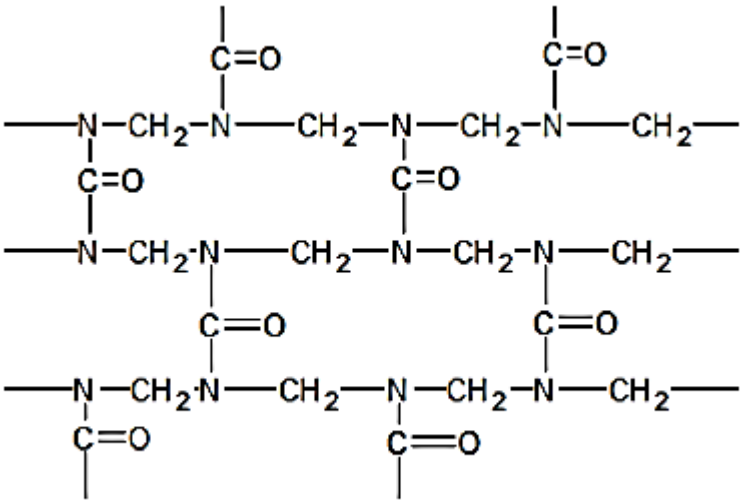

Figure 2.1 Urea formaldehyde molecular structure (Frihart, 2005)

In particleboard industry, UF adhesive is the major adhesive used, due to its exceptional properties like low production cost, great thermal stability, non-flammable and less colouring after cure (Pizzi and Mittal, 2003). However, UF adhesives are not suitable for outdoor purposes when moisture and heat exist. The presence of heat will reduce the water stability of UF adhesives. Overtime exposure to the moisture will weaken the binding properties and disintegrate the linkage, cause the releasing the formaldehyde which is hazardous. Addition of small amount of hardener could rectify the properties of UF adhesive. Example of commonly used hardener is ammonium phosphate $(NH_4)_3PO_4$.

UF based adhesive can be altered by addition of scavengers to reduce formaldehyde emissions. Melamine and hexamine were widely used as scavengers. Scavenger can decrease formaldehyde release up to two to ten times, but cannot totally stop it (Kloeser et al., 2007).

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2.4.1.2 Phenol formaldehyde adhesive

Phenol formaldehyde (PF) adhesive or also known as phenolic adhesive has commonly used for exterior composite wood products. It has better water stability as compared to urea formaldehyde thus decrease the formaldehyde emissions to 90 % less than UF (Pizzi and Mittal, 2003). Other than that, PF adhesive also showed a better thermal stability and suitable for composite wood products that subjected to high temperature application. Due to better properties and high durability, it is widely used in wood-based industry and it is second to UF adhesive as most commonly use adhesive (Zhao et al., 2011). However, the price of PF adhesive is higher as compared to other formaldehyde-based adhesive. Figure 2.2 shows the molecular structure of PF.

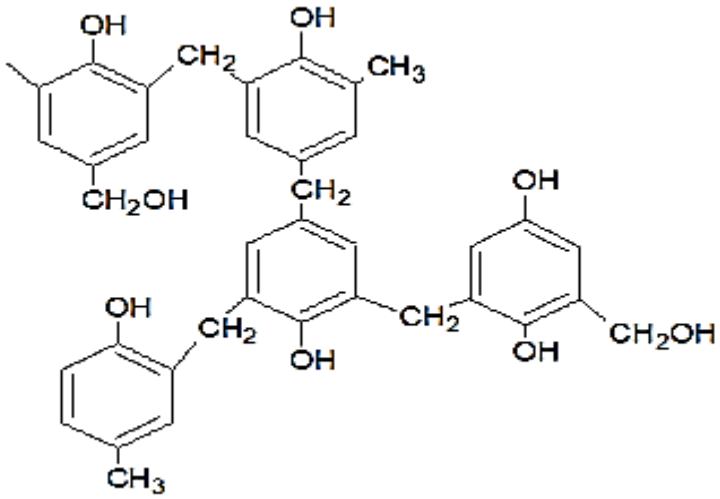

Figure 2.2 Phenol formaldehyde molecular structure (Pizzi and Mittal, 2003)

The formulation of this adhesive is based on formaldehyde, thus it sharing the same occupational exposure concerns as urea formaldehyde. Furthermore the existence of phenol in the formulation is also a concern (Zhao et al., 2011). Phenol formaldehyde recorded under NIH's Database on Hazardous Chemicals and Occupational Diseases as suspected immunotoxicant (Baumann et al., 2000).

2.4.1.3 Melamine formaldehyde adhesive

Other commonly used formaldehyde adhesive is melamine formaldehyde (MF) adhesive. Melamine formaldehyde was introduced as alternative adhesive to the Urea formaldehyde with better properties toward water, heat stain and electricity (Pizzi and Mittal 2003). Figure 2.3 shows the molecular structure of MF. In composite wood-based products, MF adhesive is particularly used for semi-exterior and exterior grade products. Similar to PF, the major drawback of MF adhesive is the higher cost of the production. Due to the high cost of MF adhesive, the application of this adhesive is specified for certain product, usually for outdoor purposes.

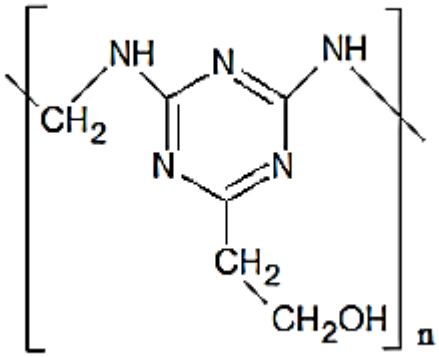

Figure 2.3 Melamine formaldehyde molecular structure (Frihart, 2005)

2.4.1.4 Formaldehyde Emission

A major problem of using formaldehyde based adhesive is the formaldehyde emission, the major indoor air pollution which is known as volatile organic compounds (VOCs) (Baumann et al., 2000). Formaldehyde is listed as hazardous compound by the California Air Resources Board (CARB) in 1992, classified due to its human carcinogenic properties with unknown harmless exposure level. (Salem et al., 2012). Exposure to the colourless gas of formaldehyde may cause a short-term irritant effect and long-term health effect like nasopharyngeal cancer and skin related disease (Bosetti et al., 2008). Those effect varies depending on the amount of formaldehyde emission, period of exposure and individual sensitivity. Wood-based products are major contributors to formaldehyde emissions, from the usage of formaldehyde-based adhesive such as urea formaldehyde, phenol formaldehyde and melamine formaldehyde. There are a many factors that influence formaldehyde emission of wood-based products, such as moisture, heat, air flow, loading ration and etc. (Salem et al., 2012). Normally, there are two way that formaldehyde emission can occur from wood composite; first is from unreacted free formaldehyde, during the curing process and second is from the decomposition of adhesive. The releasing of unreacted free formaldehyde occur during the hot pressing from manufacturing process. The level of emission is greatly affected from the types and amount of adhesives used also depend on the press condition, catalyst and moisture content.

A major causes of formaldehyde emission is due to the decomposition of the adhesive through hydrolysis (addition of water). The cured formaldehyde adhesive such as UF degrade when reacted with water. UF adhesive is chemically unstable compare to PF adhesive, it will hydrolyse under suitable condition with presences of heat and moisture. Thus wood-based composite products made from UF adhesive is

not suitable for outdoor usage. Cured PF adhesive is more stable and less hydrophilic so it tend to be less effected by hydrolysis than UF adhesive. Even though cured PF adhesive have high moisture stability, it cannot stand long-term exposure to water. Long contact with water, in the presence of elevated heat could trigger the breakdown of the adhesive.

Pressure from the public about the hazardous effect of formaldehyde emission let to the establishment of a new standard with respect to the content of UF adhesive in the wood-based product, especially particleboards (Salem et al., 2012). Many efforts have been done to reduce the application of formaldehyde adhesives. Researchers are seeking for a new kind of wood-based composite adhesive with 'green' characteristic without compromise the performance. The introducing of E_1 type particleboard is one example of effort to reduce the emission of formaldehyde. The usage of other synthetic adhesive such as polymeric methylene diphenyl diisocyanate (pMDI) help to reduce the generation of formaldehyde emission by wood-based composite industry, but in term of cost, safety and health concern it is not reliable. From previous research by Moubarik et al., (2010), adhesive from mixtures of corn starch, mimosa tannin and UF produced a particleboard with comparable physical and mechanical properties to UF bonded particleboard. Using a natural-based adhesive could be an ideal approach in order to reduce the dependence to the formaldehyde adhesive. In this study, extracted starch from oil palm trunk was modified by crosslinking process with sodium trimetaphosphate (STMP). The cross-linked STMP starch was evaluated for its potential as wood-based composite panel adhesive.

2.4.2 Natural-based adhesives

Long before the introduction of synthetic adhesives, adhesive from natural resources like soybean, protein, bones and others have been utilized (Frihart, 2005). Many synthetic adhesives for wood-based composite product were formaldehyde-based that later rise the concern about the hazardous emission of formaldehyde (Roffael, 2006). The rise of public concern towards the releasing of hazardous free formaldehyde from the hot pressing process and overtime release from the hydrolysis process of cured formaldehyde and establishment of low formaldehyde standard for wood-based composite manufacturing led the industry to seek a solution. One of the alternative solution is to utilise natural-based adhesives. With the utilisation of natural-based adhesive, wood-based composite industry will be recognize as green producer and meets the consumer needs towards the green society. A lot of studies and research have been conducted to analyse the potential and optimise the utilization of natural adhesives for producing high-quality green wood-based composites (Pizzi, 2006).

2.4.2.1 Protein-based adhesives

Proteins are characterized based on the order of 20 different amino acids linked via peptide-bonds. Those amino acids are either acidic, basic or neutral. Properties of protein adhesive are vary depending on the sources (Frihart, 2005). As an adhesive, natural protein needs to be transformed from naturally soluble proteins into an insoluble stage and this can be done through thermal exposure or by reactions with a chemical compound (Müller et al., 2007). There were several advantages of using protein as adhesive one of them is the amphoteric character that allowed protein to react as either acids or base and not dependable on certain pH-value (Müller et al., 2007). It can be linked or reacted to various types of additives. In

addition, protein can be extracted from numerous renewable resources either from plants or animals at low cost. The four main groups of low cost and highly available proteins are albumins, collagens, caseins and plant proteins (Schöpper and Kharazipour, 2006). The most commonly used protein-based adhesive is soybean flour. In the early 1900s, soybean protein adhesives were widely used for interior plywood industry and then further improved for better water resistance (Lambuth, 2003). However the improvement was not enough to make plywood from protein-based adhesives suitable for exterior application. Albumin protein extracted from beef and hogs blood have better water resistance properties but their quality are not consistant, not cheap enough, and the supply is not that plenty either (Lambuth, 2003).

2.4.1.2 Tannin-based adhesives

Tannins are natural polyphenols available in various species in plants, but vary in concentration. As result, only few species are economically viable to isolate them. As adhesives, tannins are combined with formaldehyde and use as substitution to phenol. Tannins are more reactive than phenol, however they are also more costly than phenol. The purified tannins have similar characteristic as resorcinol which is highly reactive and form water resistant bonds when polymerized with formaldehyde but have lower cross-link density (Frihart, 2005). Compared to synthetic adhesives, tannins have several disadvantages, such as highly viscosity, low and inconsistent availability, and also different reactivity.

2.4.1.3 Lignin-based adhesive

Lignin is both aromatic compound and a complex polymer. During extraction, the polymeric structure of lignin needs to be partially degraded in order to

isolate them from cellulose. For adhesive application, the partially degraded lignin, needs to further polymerization to gain useful adhesive properties. Lignin is available in huge quantities at low cost. It is by product of pulping process in papermaking (Pizzi and Mittal, 2003). Differ from tannin, lignin contains small amount of phenolic rings and no polyhydroxy phenyl rings, so the reactivity with formalin is low. Many research have been done to improve lignin's adhesion characteristic. Due lignin's low reactivity towards formaldehyde, supplementary curing mechanism have been considered, including thermal cure with acids and oxidative coupling using hydrogen peroxides and catalysts (Bertaud et al., 2012).

2.4.1.4 Starch-based adhesives

Starch is a polysaccharide polymer, constructed from repeating unit of glucose pyranose monomer ($C_6H_{10}O_5$) ranging from 300 to 1000 units (Neelam et al., 2012). The molecular structure of starch is showed in Figure 2.4. Starch exists in combination of two types of polymer known as amylose and amylopectin. Amylose is a linear form of polysaccharide polymer while amylopectin is a branched. Linear amylose is linked by α-1,4-bonds and branched amylopectin is linked by α-1,6-bonds.

Starch is stored in plant as energy source produced from photosynthesis process (Murphy et al., 2000). Starch mostly found in the seeds, fruits, tubers and pith of stems of plants, especially in corn, wheat, rice, sago and potatoes (Müller et al., 2007). It is inexpensive and largely available. In solution, amylose basically swells to a larger volume as compared to amylopectin, but in the presence of heat, amylopectin absorbs more water than amylose. Amylopectin has an infinite diversity

of structure, depends on the length of the branch and its frequency, and more amorphous as compared to amylose (Wool and Sun, 2011).

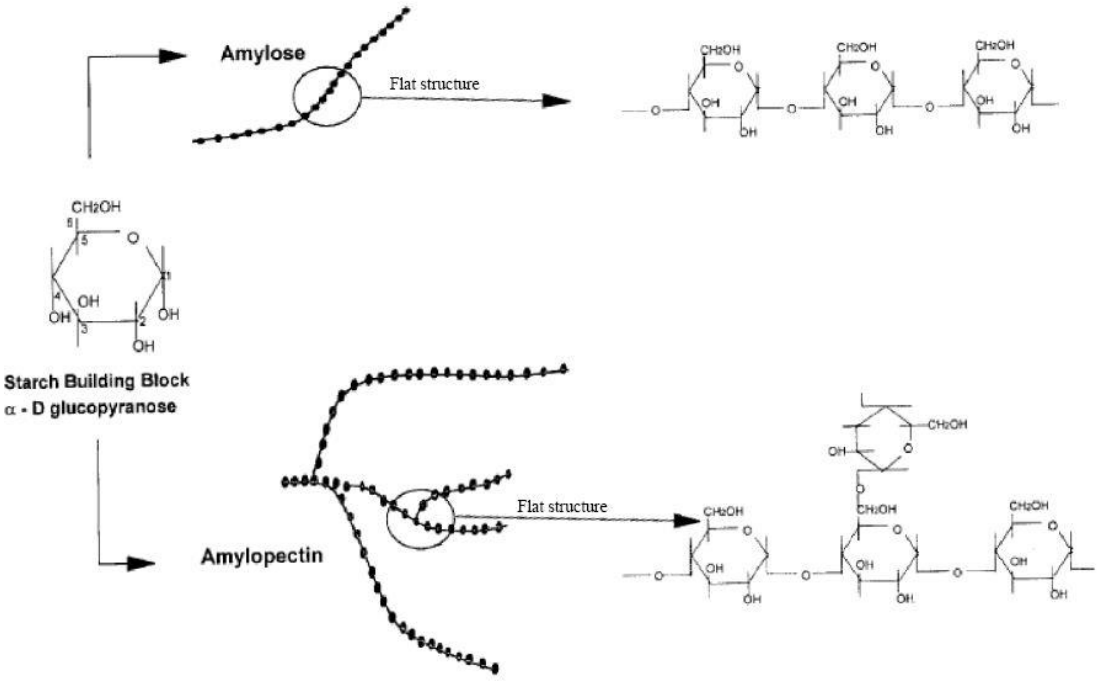

Figure 2.4 Molecular structure of starch (Murphy et al., 2000).

Industrial starch is generally used as filler in paper industry. It is also mixed with several types of conventional adhesives as an extender to reduce the amount of synthetic resin, the emission of formaldehyde and the production cost (Pan et al., 2006). In addition, starch acts as scavenger for free formaldehyde (Basta et al., 2006). Starch adhesive react brilliantly with polar material like cellulose (Müller et al., 2007). However, the main disadvantage of starch adhesive is, it produces low water resistant products (Basta et al., 2006).

2.5 Oil palm trunk starch

Oil palm (*Elaeis guineensis)* was known as one of the most rapid expanding commodities (Fitzherbert et al., 2008). It was first introduced to Malaysia on late 1800s, but first commercially planted in Peninsular Malaysia in 1917 (Corley and Tinker, 2008). Malaysian oil palm plantations were expanding rapidly between 1990 and 2005 which increasing from 1.8 million hectares to 4.2 million hectares (Fitzherbert et al., 2008), and in 2011 Malaysia oil palm plantation cover about 4.917 million hectares of land area (Nadhari et al., 2014). Oil palm is Malaysian most valuable crop and being used in various fields, such as food industry, cosmetics and also for bio-fuel production (Sulaiman et al., 2012).

Trees of 25 to 35year old are considered less economic to be harvested due to low yield and harvesting process is time consuming and difficult as the trees are too high. Those trees will be chopped down and left to decay. The oil palm trunk take time to decay, this disposal method is slow because oil palm trunks take time to decay and may affect the replanting process. Many studies have been done in order to convert the oil palm waste, such as the oil palm trunks, fronds and empty fruit bunches into valuables. The potential of oil palm trunk to be utilized as the raw material for binderless composite have been done (Nadhari et al., 2014). In this study, binderless particleboard showed a satisfied performance in term of strength and dimensional stability. Other than that, previous work by Sulaiman et al., (2012) has evaluated the utilization of oil palm trunk as a source for compressed wood. The usage of oil palm trunk as new source for compressed wood reduce the production cost as the raw material is abundantly available. However, the supply of oil palm trunks is not constant making the production of oil palm trunk-based composites or compressed wood difficult.

In this research, oil palm trunk waste was utilized as source of starch. Starch was extracted from oil palm trunk and used as adhesive in three-layer particleboard manufacturing.

2.6 Starch modification

Generally, unmodified starches are chemically weak and had limited application (Murphy et al., 2000). Starch can be modified, physically, chemically, genetically and enzymatically, with general aim to produce starch derivatives with better physicochemical and structural behaviours. (Kavlani et al., 2012). Production of new starch derivatives extends the starch application and uses. The characteristic of starch depend on the modification type and tailored to suit the final applications.

In enzymatic modification, starch molecule will be expose to the specific enzyme for modification, causing hydrolization which is likely to create more functional derivatives (Neelam et al., 2012). There were previous research done using various types of enzyme for starch modification. Kim and Robyt (2000) have studied the effect of Cyclomaltodextrin glucanosyltransferase (CGTase, EC 2.41.19) mixed with isoamylase to the waxy maze starch granules. As the result, novel material with starch granules and Cyclomaltodextrins properties were produced. Genetic modification can be carried out through conventional plant-breeding or via biotechnology technique (Neelam et al., 2012). The most common modification are by physical and chemical techniques, which are discussed later.

2.6.1 Physical Modifications

Generally, physical modification of starch is done to change the structure of starch granules and convert them into cold water-soluble starch. This technique does not involve any chemical that maybe harmful to human use (Neelam et al., 2012). Table 2.2 show some example of physical modification technique of starch and it their derivative properties.

Table 2.2 Some examples of physical modification techniques of starch and their derivative properties

Types of physical modification	Starch derivative properties
1. Hydrothermal Treatment (HTM)	Decrease starch paste solubility and viscosity (Yadav et al., 2013). Decrease starch swelling and amylose leaching (Putri et al., 2014)
2. Annealing	Reduce swelling capacity, solubility and viscosity of starch (Yadav et al., 2013).
3. Pre-gelatinisation	Delay the starch retrogradation (Wu et al., 2010) Increase starch viscosity, solubility and swelling capacity (Neelam et al., 2012)

2.6.2 Chemical modifications

Chemical modifications are the most common techniques used, they were applied in various applications such as paper making industry, adhesives, textiles and food. These technique usually involving the introduction of new functional groups to starch structure, thus altered the physico-chemical properties of starch (Neelam et al., 2012). Cross-linking is the main chemical modification in the starch industry. It enhances the bonding of starch molecules by adding or replacing the hydrogen bonding molecule with stronger and permanent covalent bond (Murphy et al., 2000).

Table 2.3 Some examples of chemical modification techniques of starch and their derivative properties

Types of chemical modifications	Starch derivative properties
1. Etherification and esterification	Decrease starch gelatinization and swelling (Neelam et al., 2012)
2. Cross-linking	Extend the degree of polymerization (Alcázar-Alay and Meireles, 2015). Decrease paste clarity of starch and swelling capacity (Koo et al., 2010).
3. Oxidation	Decrease viscosity and thermal stability and starch retrogradation (Neelam et al., 2012). Reduce starch paste viscoelastic properties (Ptaszek et al., 2013).
4. Cationization	Decrease paste temperature and increase starch viscosity (Neelam et al., 2012). Decrease size of starch granule and fragmentation (Liu et al., 2014).
5. Acetylation	Lessen the bond resistance between starch molecules, extend starch swelling capacity and solubility (Berski et al., 2011). Convert hydroxyl groups and anhydrous glucose in starch to acetylated groups (Huang et al., 2010).
6. Acid hydrolysis	Develop gel consistency of starch, starch depolymerisation and decrease paste viscosity (Ulbrich et al., 2015).